High Laser Damage Threshold Porous Silica
Antireflective Coating

I. M. Thomas

This paper was prepared for submittal to
Applied Optics

December 2, 1985

DISCLAIMER

HIGH LASER DAMAGE THRESHOLD POROUS SILICA
ANTIREFLECTIVE COATING

I. M. Thomas*

Lawrence Livermore National Laboratory
Livermore, California

ABSTRACT

A quarterwave-thick, narrow-bandwidth, antireflective coating for fused silica optical components and KDP crystals has been developed. The coating consists of porous silica prepared from a silica sol in ethanol. It is applied by dip or spin from a solution at room temperature and requires no further treatment. The laser damage threshold levels are about equal to the surface damage thresholds of the uncoated substrates.

Introduction

Surfaces of transmitting optical components of high power lasers require coatings or other treatment to reduce their reflectivity and the attendant loss. Laser-induced damage to traditional multilayer, thin-film, antireflective (AR) coatings usually limits the laser's maximum power.

We have previously shown that porous silica surface layers are capable of rendering antireflective surfaces with substantially higher resistance to laser-induced damage than traditional AR coatings. [1-3] Such surfaces have been produced by acid leaching of phase-separated[4] and non phase-separated[5] borosilicate glass; the latter process developed by Schott Optical Technologies, Inc., and called the Neutral Solution Process, is currently used on borosilicate optics for the 100 kJ Nd-glass laser Nova at Lawrence Livermore National Laboratory.

More recently, we have investigated the use of porous silica as an AR coating which can be applied to a wide variety of optical and nonlinear optical materials not treatable by the earlier processes. The use of porous silica as an AR coating is well known; acid neutralized sodium silicate[6] and silica sols[7,8] have been used on glass substrates to produce films of varying degrees of effectiveness. Both of these are aqueous systems and use commercially available materials. Some work has also involved the use of organic silicates as the silica source.[9] These materials are readily hydrolyzed to silica and have been applied as acid catalyzed partially hydrolyzed products in organic solution to give porous coatings after exposure to water and heat. A somewhat more complicated system has been developed in which a sol-gel process was used to deposit a multi-component glass film of a composition that could phase separate; the film was then heated to cause phase separation and one phase was preferentially removed by leaching and etching to leave the second phase as a porous high silica containing film.[3,10]

Because of the special nature of coatings required for laser applications, particularly damage resistance, our investigation has involved the use of organic silicates, specifically tetraethyl orthosilicate, $Si(OC_2H_5)_4$, as the silica source. This material is a volatile liquid which can readily be purified by fractional distillation: silica obtained by hydrolysis retains the high purity level and thus laser damage due to impurities is minimized.

$$Si(OC_2H_5)_4 + 2H_2O \rightarrow SiO_2 + 4C_2H_5OH.$$
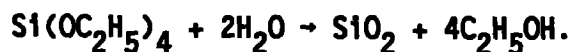
The hydrolysis of ethyl silicate requires either an acidic or basic catalyst and the intermediate products are quite different in each case. Acid catalysis initially gives a soluble polyethoxysiloxane; at this stage it can be applied to a substrate and subsequent heat treatment to 450°C to decompose organic entities is required to form porous SiO_2. The porosity of this coating can be increased if necessary by an HF etch.[9] When we investigated this process the AR properties were quite satisfactory but we experienced low laser damage thresholds in some cases; this was possibly due to carbonaceous residues left in the coating from incomplete removal of organic material during the heat treatment.

When a base catalyst is used for hydrolysis, a colloidal suspension of silica particles is formed directly at room temperature and these particles are substantially free of organic entities. When this suspension is applied to a substrate, a porous silica coating consisting of layers of silica particles is obtained after evaporation of the solvent. This coating, in contrast to the acid catalyzed material, contains a minimum of organic residues and is not heated; carbonaceous by-products are therefore not present and high laser damage thresholds result. In this investigation, the base catalyzed system was used exclusively.

The particle size can be varied from approximately 5 nm to about 2 microns by changing water, base catalyst or silica concentrations or by variation in the solvent. In this investigation ethanol was normally used as the solvent with a slight excess of water and ammonia as catalyst; this resulted in substantially uniform particles approximately 20 nm in diameter.

2. Experimental

Tetraethyl orthosilicate was fractionally distilled under nitrogen using a 120 cm vacuum jacketed and silvered Vigreux glass column fitted with an infinitely variable distillation head. The fraction boiling at 166-167°C was collected and was stored in glass bottles under nitrogen prior to use.

A typical coating sol was prepared by the base catalyzed hydrolysis of the distilled product by a method similar to that described by Stober[11] as follows. Concentrated ammonium hydroxide solution (57% analytical reagent, 9.6 g) was added to a solution of tetraethyl silicate (31.2 g) in anhydrous ethyl alcohol (259 g) with stirring at room temperature. The reaction mixture was then allowed to stand at room temperature for three days to allow hydrolysis and sol formation to be completed. The final product consisted of a colloidal suspension of SiO_2 particles in substantially anhydrous ethanol at a concentration of 3.0%. Transmission electron microscopy indicated the silica particles were approximately spherical with a diameter of about 20 nm.

Coating sols of different silica content were prepared by variation in the quantities of silicate and ammonium hydroxide solution; in addition, some sols were prepared in methanol rather than ethanol. The performance of all these materials was similar.

Coating was carried out either by a spin or dip process. Samples were coated at room temperature and then air dried; no further treatment was required. For AR coatings optimized for 350 nm wavelength light, a withdrawal rate of 5 cm/min was suitable for the dip process. Spinning was carried out at 350 rpm and required ethanol dilution of a 3% silica coating sol to 0.75% silica. Thicker coatings for longer wavelength light were obtained by multidip or spin with air drying in between.

The results described in the next section were obtained on 5 cm diameter by 1 cm thick polished fused silica substrates and on 5 cm x 5 cm x 1.75 cm potassium dihydrogen phosphate (KDP) crystals with diamond-turned surfaces.[12] Fused silica focussing lenses of 80 cm diameter and 27 cm square KDP crystals are now coated routinely and their performance is similar to that reported for the smaller samples.

Discussion of Results

Transmission spectra of coatings on fused silica and KDP substrates are shown in Figs. 1 and 2. These spectra are characteristic of quarterwave AR coatings of refractive index corresponding to the relationship $n_c = \sqrt{n_1 n_2}$ where n_c is the index of the coating, n_1 is the index of air, and n_2 is the index of the substrate. Appropriate substitution indicates that the index of the coating is approximately 1.22. Further calculation then shows that the silica particles must be stacked to give an average porosity of about 50%.

It is interesting to note that the densest possible packing of uniform spheres gives a porosity of only 26%. We must therefore conclude that the slight variations in particle size and shape and also possible particle porosity contribute to the increased porosity of coatings obtained from them.

The effect of multicoats on fused silica substrates is also illustrated in Fig. 1. This figure shows the transmission of the substrate when given successive coats of a sol containing 2.24% silica at a withdrawal rate of 3 cm/minute. Samples were air dried at room temperature between coats. Transmittance of about 100% was measured at 370 nm and at 550 nm after application of, respectively, the second and third coating layers. At the minima, transmittance of the coated substrate was equal to the bare substrate. The refractive index of the coating was therefore homogeneous, not graded. The coating with peak transmission at 550 nm had optical thickness of 137.5 nm which implies that about 46 nm of optical thickness was added during each coating application. A coating with a thickness of 92 nm (two layers) would have peak transmission at 368 nm while a single layer would be transmissive at 184 nm. These values are consistent with the measured spectra, scattering in the coating and absorption in the substrate displacing the predicted 184 nm transmission maximum to 220 nm.

We have found that thicker coatings can also be obtained by increasing the silica content in the coating sol.

Figure 3 gives laser damage thresholds measured at three different laser wavelengths and pulse durations for the sol coatings on fused silica substrates, and that measured at one laser wavelength for the coatings on KDP substrates. The 248-nm threshold was measured by Foltyn at Los Alamos National Laboratory. These thresholds were measured on coatings whose thicknesses were arranged such that maximum transmission occurred at the measurement wavelengths. The thresholds obtained approximately equal the thresholds measured for the uncoated substrate surfaces.[13]

Summary

A method has been developed to prepare porous silica AR coatings on silica or KDP substrates. This involves the preparation of a silica sol in ethanol from a high purity organic silicate starting material and application of this sol, by spin or dip, to substrates at room temperature followed by an air dry. No further processing is required and coatings with high laser damage thresholds and excellent optical performance are obtained.

Acknowledgements

References

1. W. H. Lowdermilk and D. Milam, "Graded-index antireflection surfaces for high power laser applications", Appl. Phys. Lett. 36, 891 (1980).

2. L. M. Cook, W. H. Lowdermilk, D. Milam and J. E. Swain, "Antireflective surfaces for high energy laser optics formed by neutral solution processing", Appl. Opt. 21, 1482 (1982).

3. S. P. Mukherjee and W. H. Lowdermilk, "Gradient-index AR film deposited by the sol-gel process", Appl. Opt. 21, 293 (1982).

4. M. J. Minot, "Single-layer, gradient refractive index antireflection films effective from 0.35 to 2.5 μm", J. Opt. Soc. Am. 66, 515 (1976).

5. L. M. Cook, K.-H. Mader and R. Schnabel, "Integral antireflective surfaces on silicate glass", U. S. Pat. Appl. 309,149, October 5, 1981.

6. E. M. Pastirik and M. C. Keeling, "A low cost durable anti-reflective film for solar collectors", 13th IEEE Proton. Spec. Conf., Washington, D.C., June 1978.

7. H. R. Moulton, "Composition for reducing the reflection of light", U.S. Pat. 2,601,123 (1952).

8. H. R. Moulton, "Method of producing thin microporous silica coatings having reflection reducing characteristics and the articles so coated", U.S. Pat. 2,474,061 (1949).

9. B. Yoldas and D. P. Partlow, "Wide spectrum antireflective coatings for fused silica and other glasses", Appl. Opt., 23, 1418 (1984).

10. H. L. McCollister and N. L. Boling, "Process of making glass articles having antireflective coatings and product", U.S. Pat. 4,273,826 (1981).

11. W. Stober, A. Fink and E. Bohn, "Controlled growth of monodisperse silica spheres in the micron size range", J. Coll. and Inter. Sci. 26, 62 (1968).

12. M. A. Summers, B. C. Johnson and J. D. Williams, 1982 Laser Program Annual Report, Lawrence Livermore National Laboratory UCRL-50021-82, p. 2-7 (1983).

13. M. C. Staggs and F. Rainer, "Damage thresholds of fused silica, plastics and KDP crystals measured with 0.6 ns, 355 nm pulses", Nat. Bur. Stand. (U.S.) Spec. Publ. 1985 (in press). Also W. H. Lowdermilk and D. Milam, "Review of ultraviolet damage threshold measurements at Lawrence Livermore National Laboratory", SPIE Vol. 476, Excimer Lasers Their Applications and New Frontiers in Lasers, p. 143 (1984).

2129R

Figure Captions

1. Transmittance of coatings on fused silica substrates.
2. Transmittance of coatings on diamond-turned KDP substrates.
3. Laser damage thresholds.

2129R

Transmission spectrum of porous silica HR coating on fused silica is controlled by coating's thickness

Figure 1

Transcription of KDP

Lower curve — uncoated
Upper curve — one coat
of 3.2 % silica sol
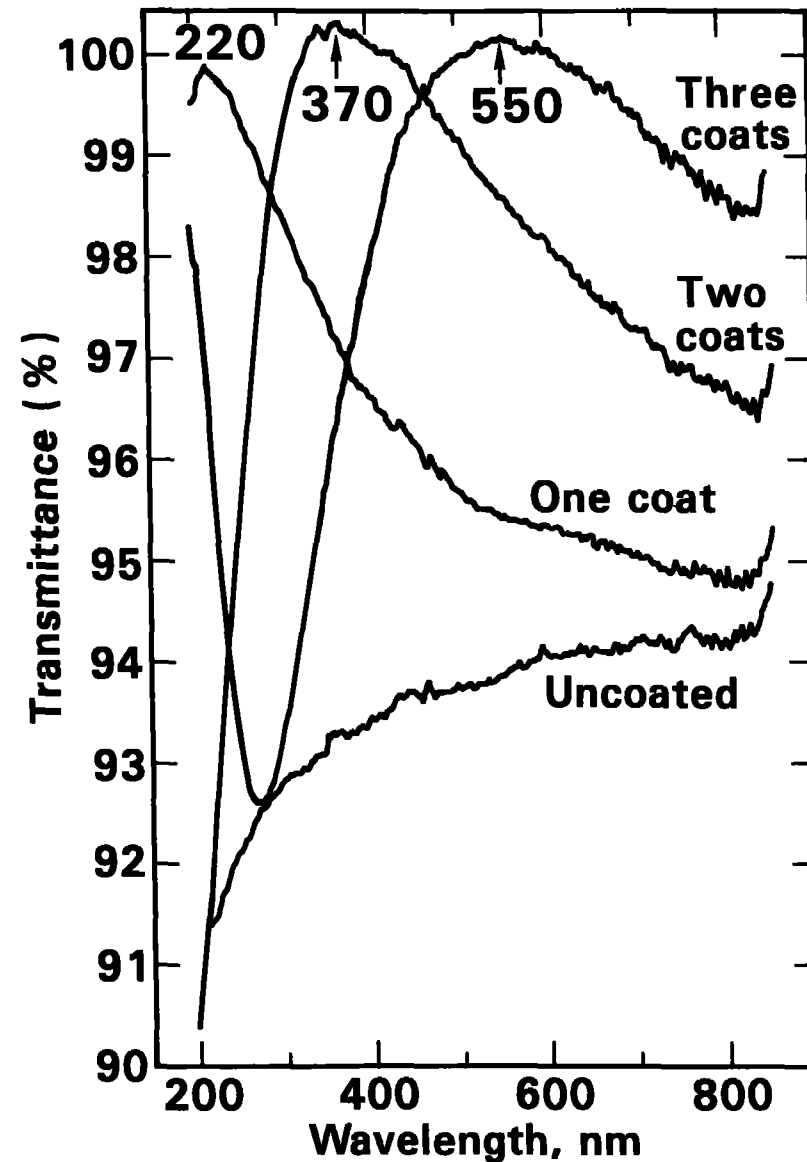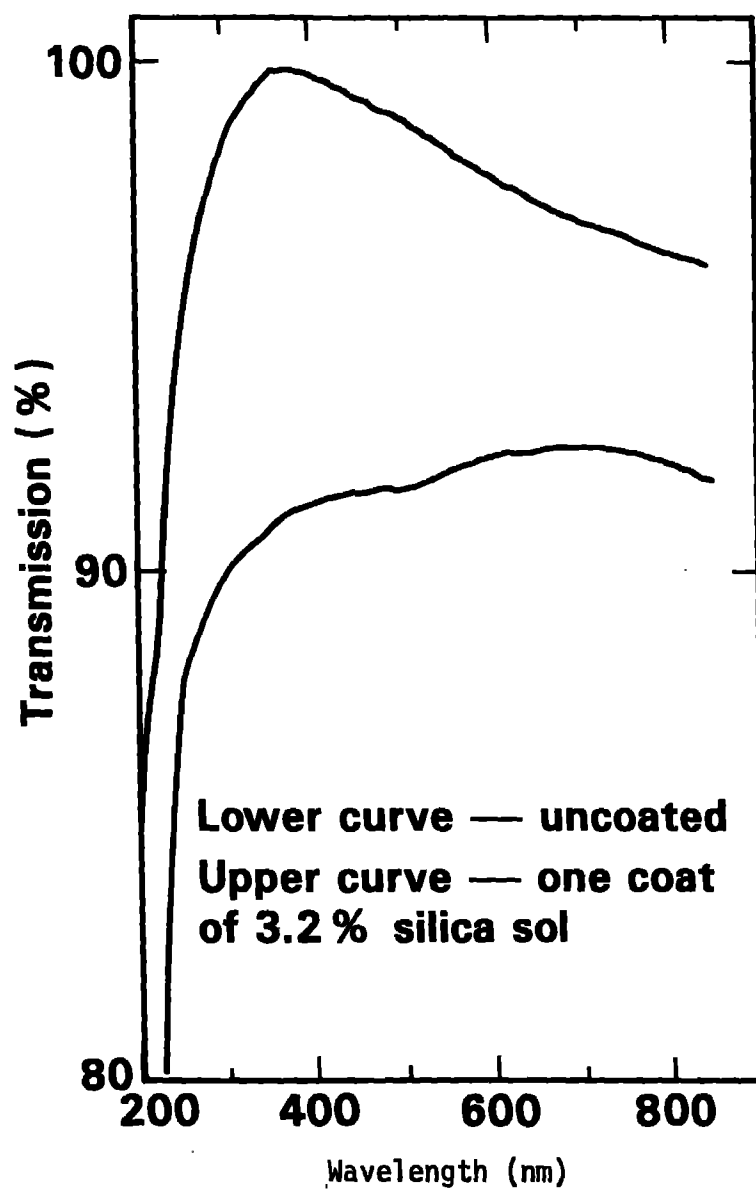
02-50-0684-1842

Figure 2

Typical damage threshold levels

Laser	SiO_2 substrate	KDP substrate
248 nm, 15 ns pulse	4 - 5 J/cm^2	
355 nm, 0.6 ns pulse	8.5 - 10 J/cm^2	$> 4 - 5$ J/cm^2
1064 nm, 1.0 ns pulse	10 - 14 J/cm^2	

Figure 3